

EA04 Analytical Chemistry Homework Assignment Due Week 6

**10-2. Calculate the pH of (a)  $1.0 \times 10^{-3}$  M HBr; (b)  $1.0 \times 10^{-2}$  M KOH.**

a)  $\text{pH} = -\log(1.0 \times 10^{-3}) = 3.00$

b)  $\text{pOH} = -\log(1.0 \times 10^{-2}) = 2.00$ ;  $\text{pH} = 14.00 - \text{pOH} = 12.00$

**10-4a. The measured pH of 0.0100 M HCl at 25°C is 1.092. From this information, calculate the activity coefficient of  $\text{H}^+$  and compare your answer to that in Table 8-1.**

$$\begin{aligned} \text{pH} = -\log[\text{H}^+] \gamma_{\text{H}^+} &\rightarrow 1.092 = -\log\{(0.100) \gamma_{\text{H}^+}\} \\ 10^{-1.092} &= 0.100 \gamma_{\text{H}^+} \rightarrow 0.0809 = 0.100 \gamma_{\text{H}^+} \\ \gamma_{\text{H}^+} &= 0.809 \end{aligned}$$

Value in Table 8-1 is 0.83 for 0.1 M  $\text{H}^+$ . Fairly close.

**10-8. Find the pH and concentrations of  $(\text{CH}_3)_3\text{N}$  and  $(\text{CH}_3)_3\text{NH}^+$  in a 0.060 M solution of trimethylammonium chloride.**

The ammonium ion is the acid and the amine is its conjugate base.  $K_a = 1.58 \times 10^{-10}$ .

Write the chemical equation  $(\text{CH}_3)_3\text{NH}^+ \rightleftharpoons (\text{CH}_3)_3\text{N} + \text{H}^+$

$K_a = x^2 / (0.060 - x)$  assume  $x$  small compared to 0.060

$$x^2 = 1.58 \times 10^{-10} \times 0.060 \rightarrow 3.08 \times 10^{-6} \text{ M (which is small compared to 0.060)}$$

$$\text{pH} = -\log(3.08 \times 10^{-6}) = 5.51$$

**10-11. A 0.0450 M solution of benzoic acid has a pH of 2.78. Calculate pKa for this acid.**

Equation  $\text{C}_6\text{H}_5\text{CO}_2\text{H} \rightleftharpoons \text{C}_6\text{H}_5\text{CO}_2^- + \text{H}^+$

The concentration of benzoate and  $\text{H}^+$  are  $x = 10^{-2.78} = 1.66 \times 10^{-3}$  M

$$K_a = x^2 / (F - x) = (1.66 \times 10^{-3})^2 / (0.0450 - 0.00166) = 6.35 \times 10^{-5} \rightarrow \text{pKa} = 4.20$$

Value in Table G is 4.202

**10-20 Find the pH of 0.050 M NaCN.**

The cyanide ion is the conjugate base of HCN.

$$K_b = K_w / K_a = 1.0 \times 10^{-14} / 6.2 \times 10^{-10} = 1.61 \times 10^{-5} \quad \text{Remember } x = [\text{OH}^-] \text{ for a base.}$$

$$K_b = x^2 / (F - x) = x^2 / (0.050 - x) = 1.61 \times 10^{-5} \rightarrow x = 8.97 \times 10^{-4}$$

Try a second approximation

$$K_b = x^2/(F - x) = x^2/(0.050 - 0.000897) = 1.61 \times 10^{-5} \rightarrow x = 8.89 \times 10^{-4}$$

To 2 sig figs we get  $[\text{OH}^-] = 8.9 \times 10^{-4} \text{ M} \rightarrow \text{pOH} = 3.05 \quad \text{pH} = 14.00 - 3.05 = 10.95$

**10.32. A buffer was prepared by dissolving 0.100 mol of the weak acid HA ( $K_a = 1.00 \times 10^{-5}$ ) plus 0.050 mol of its conjugate base  $\text{Na}^+\text{A}^-$  in 1.00 L. Find the pH.**

We have a buffer problem with  $[\text{HA}] = 0.100 \text{ M}$  and  $[\text{A}^-] = 0.050 \text{ M}$

$$\text{pH} = \text{p}K_a + \log [\text{A}^-]/[\text{HA}] = 5.000 + \log \{0.050/0.100\} = 5.000 - 0.30 = 4.70$$

**10.39 Calculate how many milliliters of 0.626 M KOH should be added to 5.00 g of HEPES (Table 10-2) to give a pH of 7.40.**

HEPES has a  $\text{p}K_a$  of 7.56 and a formula mass of 238.306 g/mol. We have  $5.00/238.306 = 0.02098$  mol of HEPES to work with.

We are preparing a HEPES buffer by adding hydroxide to convert HA to  $\text{A}^-$ . The chemical equation is



We use the H-H equation to get the ratio of acid and conjugate base at the desired pH

$$\text{pH} - \text{p}K_a = \log [\text{A}^-]/[\text{HA}] \rightarrow 7.40 - 7.56 = -0.16 = \log \text{ratio} \rightarrow [\text{A}^-] = 0.6918 [\text{HA}]$$

since the volume will be the same this is also the mol ratio.

We also know that  $\text{mol A}^- + \text{mol HA} = 0.02098$  or  $\text{mol HA} = 0.02098 - \text{mol A}^-$

$$\text{So mol A}^- = 0.6918 (0.02098 - \text{mol A}^-) \rightarrow 1.6918 \text{ mol A}^- = 0.01451 \rightarrow \text{mol A}^- = 0.01451/1.6918$$

$\text{mol A}^- = 8.58 \times 10^{-3}$ . Since each mol of  $\text{OH}^-$  that reacts produces a mol of  $\text{A}^-$ , this is the number of moles of hydroxide that we need.

$$8.58 \times 10^{-3} \text{ mol OH}^- \times 1.00 \text{ L} / 0.626 \text{ mol OH}^- = 0.01370 \text{ L} \text{ or } 13.7 \text{ mL of KOH solution.}$$

**1. Calculate the hydrogen ion concentration in 0.120 M nitrous acid.**

This is the solution of a weak acid.

$$K_a = 7.1 \times 10^{-4} = x^2/(F - x)$$

This can be solved by the quadratic equation or by approximation. Let's use approximation by assuming  $x$  small compared to  $F$

$$x^2 = K_a F = 7.1 \times 10^{-4} \times 0.120 \rightarrow x_1 = 9.23 \times 10^{-3} \quad \text{what limits the sig figs in answer?}$$

so  $x$  is  $9.23 \times 10^{-3} / 0.120 = 8\%$  of  $F$ .

$$\text{Now set } [\text{HNO}_2] = 0.120 - 9.23 \times 10^{-3} = 0.11077$$

$$x^2 = K_a F = 7.1 \times 10^{-4} \times 0.11077 \rightarrow x_2 = 8.86 \times 10^{-3} \text{ M}$$

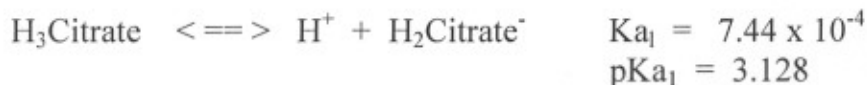
a third round gives

$$x^2 = K_a F = 7.1 \times 10^{-4} \times 0.11114 \rightarrow x_3 = 8.88 \times 10^{-3} \text{ M}$$

or  $x = 8.9 \times 10^{-3} \text{ M}$  since our answer should be to only 2 sig figs.

**2. Calculate the hydrogen ion concentration for a buffer solution that is 0.200 M in citric acid and 0.150 M in sodium dihydrogen citrate.**

The principal equilibrium in this solution is the dissociation of citric acid.



$$\text{pH} = \text{p}K_a + \log [\text{H}_2\text{Citrate}^-] / [\text{H}_3\text{Citrate}]$$

$$\text{pH} = 3.128 + \log 0.150 / 0.200 = 3.128 - 0.125 = 3.003$$

**3. (11-5) We will abbreviate malonic acid,  $\text{CH}_2(\text{CO}_2\text{H})_2$ , as  $\text{H}_2\text{M}$ . Find the pH and concentrations of  $\text{H}_2\text{M}$ ,  $\text{HM}^-$  and  $\text{M}^{2-}$  in (a) 0.100 M  $\text{H}_2\text{M}$ ; (b) 0.100 M  $\text{NaHM}$ ; (c) 0.100 M  $\text{Na}_2\text{M}$ . [If you are interested, use the method of Box 11-1 for part (b).]**

We first need the  $K_a$ 's.  $K_{a1} = 1.42 \times 10^{-3}$   $\text{p}K_{a1} = 2.847$   
 $K_{a2} = 2.01 \times 10^{-6}$   $\text{p}K_{a2} = 5.696$

(a) This is the acid solution  $x^2 = K_{a1} (F-x) = 1.42 \times 10^{-3} (0.100 - x)$  assume  $x$  small

$$x_1 = 0.0119$$

$$\text{try again } x^2 = 1.42 \times 10^{-3} (0.100 - 0.0119) = 1.25 \times 10^{-4}$$

$$x_2 = 0.0112$$

$$\text{last time try again } x^2 = 1.42 \times 10^{-3} (0.100 - 0.0112) = 1.26 \times 10^{-4}$$

$$x_2 = 0.0112$$

$$[\text{HM}^-] = [\text{H}^+] = 0.0112 \text{ M}; \quad \text{pH} = 1.951$$

$$[\text{H}_2\text{M}] = (0.100 - 0.0112) = 0.089 \text{ M} \quad \text{Why only 2 sig figs?}$$

$$K_{a2} = \frac{[\text{H}^+][\text{M}^{2-}]}{[\text{HM}^-]} \rightarrow [\text{M}^{2-}] = K_{a2} * [\text{HM}^-] / [\text{H}^+] = 2.01 \times 10^{-6} * 0.0112 / 0.0112$$

$$[\text{M}^{2-}] = 2.01 \times 10^{-6}$$

(b)  $[HM^-] = F = 0.100 \text{ M}$

$$[H^+] = \frac{\sqrt{K_{a1}K_{a2}F + K_{a1}K_w}}{K_{a1} + F}$$

$$[H^+] = \frac{\sqrt{1.42 \times 10^{-3} * 2.01 \times 10^{-6} * 0.100 + 1.42 \times 10^{-3} * 1.0 \times 10^{-14}}}{\sqrt{1.42 \times 10^{-3} + 0.100}}$$

$$= \{ (2.85 \times 10^{-10} + \text{small}) / 0.101 \}^{1/2}$$

$$[H^+] = 5.32 \times 10^{-5} \text{ M} \quad \text{pH} = 4.274$$

our other method was  $\text{pH} = \frac{1}{2} (2.847 + 5.696) = 4.272$

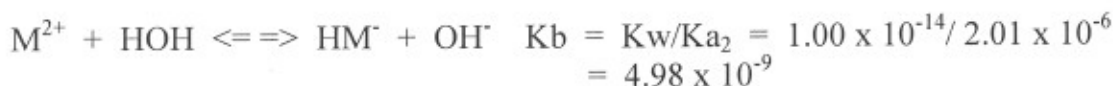
$$[M^{2-}] = K_{a2} * [HM^-] / [H^+] = 2.01 \times 10^{-6} * 0.100 / (5.32 \times 10^{-5}) = 3.78 \times 10^{-3} \text{ M}$$

We should be at the point where  $[H_2M] = [M^{2-}]$ . Let's try the calculation and see.

$$K_{a1} = \frac{[H^+][HM^-]}{[H_2M]} \rightarrow [H_2M] = \frac{[H^+][HM^-]}{K_{a1}} = 5.32 \times 10^{-5} * 0.100 / 1.42 \times 10^{-3}$$

$$[H_2M] = 3.75 \times 10^{-3} \text{ M} \text{ pretty close}$$

(c) This system can be solved as a base.



$$0.100 - x \qquad \qquad x \qquad \qquad x$$

$$x^2 = 4.98 \times 10^{-9} (0.100 - x) \text{ assume small}$$

$$x = 2.23 \times 10^{-5} \text{ is indeed small}$$

$$[HM^-] = [OH^-] = 2.23 \times 10^{-5} \text{ M} \quad \text{pOH} = 4.652 \quad \text{pH} = 14.000 - 4.652 = 9.348$$

$$[H^+] = 10^{-9.348} = 4.48 \times 10^{-10}$$

$$[H_2M] = [H^+][HM^-] / K_{a1} = 4.48 \times 10^{-10} * 2.23 \times 10^{-5} / 1.42 \times 10^{-3}$$

$$[H_2M] = 7.04 \times 10^{-12} \text{ M}$$

**4) (11-11) How many grams of  $\text{Na}_2\text{CO}_3$  (FW 105.99) should be mixed with 5.00 g of  $\text{NaHCO}_3$  (FW 84.01) to produce  $1.00 \times 10^2 \text{ mL}$  of buffer with pH 10.00?**

This problem can be solved several ways. If we start with the Henderson-Hasselbalch equation we can solve for the ratio of the moles of base to acid and then from the moles of

conjugate acid determine the moles of conjugate base. Or we can solve the problem in one step by putting the unknown directly in the H-H equation.

the pKa is for the second dissociation of carbonic acid  
which is  $pK_{a2} = 10.329$

$$10.0 = 10.329 + \log [\text{ratio}] \rightarrow \log [\text{ratio}] = -0.329 \rightarrow [\text{ratio}] = 10^{-0.329} = 0.4688$$

$$\text{moles conjugate acid} = 5.00 \text{ g HCO}_3^- \times 1 \text{ mole} / 84.01 \text{ g} = 0.0595 \text{ mol HCO}_3^-$$

$$\text{moles conjugate base} = x \text{ g Na}_2\text{CO}_3 \times 1 \text{ mol} / 105.99 \text{ g} = x / 105.99$$

$$[\text{CO}_3^{2-}] = [\text{HCO}_3^-] * [\text{ratio}]$$

$$x = 0.0595 \text{ mol} * 0.4688 * 105.99 = 2.96 \text{ g Na}_2\text{CO}_3$$

**OR**

$$\text{pH} = \text{pKa} + \log [\text{CO}_3^{2-}] / [\text{HCO}_3^-]$$

$$10.0 = 10.329 + \log [x / 105.99] / [5.00 / 84.01]$$

$$-0.329 = \log 0.1585x = \log 0.1585 + \log x = -0.800 + \log x$$

$$\log x = 0.471 \quad x = 10^{0.471} = 2.96 \text{ g Na}_2\text{CO}_3$$

**5) (11-23) The diprotic acid H<sub>2</sub>A has pK<sub>a1</sub> = 4.00 and pK<sub>a2</sub> = 8.00.**

- At what pH is  $[\text{H}_2\text{A}] = [\text{HA}^-]$ ?
- At what pH is  $[\text{HA}^-] = [\text{A}^{2-}]$ ?
- Which is the principal species at pH 2.00?
- Which is the principal species at pH 6.00?
- Which is the principal species at pH 10.00?

This should be pretty easy if you have understand then concept of ladder diagrams and the H-H equation.

- 4.00
- 8.00
- H<sub>2</sub>A
- HA<sup>-</sup>
- A<sup>2-</sup>